

PREPARATION AND REACTIONS OF ISOCYANATES OF SULFURIC AND PHOSPHORIC ACID

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Abstract

Various syntheses of the diisocyanate of sulfuric acid will be described. Its properties and reactions with proton-active materials will be discussed. Reaction with glycols and with diamines leads to the formation of polymeric sulfo-urethanes and sulfo-ureas which, however, are only slightly stable towards hydrolysis. Further, a new synthesis of phosphorus oxytriisocyanate will be mentioned.

Organic diisocyanates have long served as important starting materials for the preparation of polymers, of which the polyurethanes especially have attained significance in technical fields. Inorganic poly-isocyanates on the other hand were until recent times only seldom described in the literature and relatively little was known about their reactions.

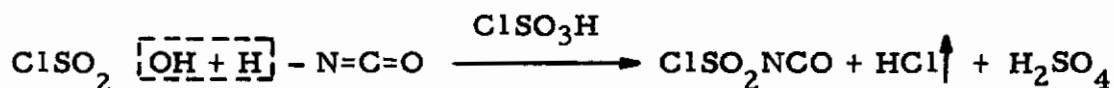
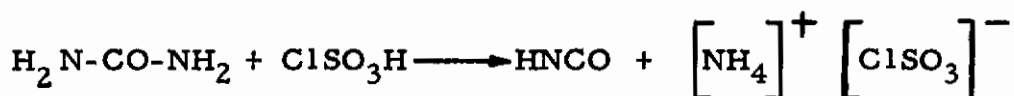
We thus commenced three years ago with a program of research directed primarily towards the preparation of the isocyanates of sulfuric acid for the purpose of studying their poly-addition reactions with lower alcohols and with amines. In this manner, we hoped to gain access to polymeric sulfo-urethanes and sulfo-ureas.

The preparation of sulfuryl diisocyanate was accomplished with the assistance of chlorosulfonylisocyanate. This compound can be easily prepared in the reaction between cyanogen chloride and sulfur trioxide according to R. Graf¹:



We found that a further convenient procedure consists in the reaction of urea with chlorosulfonic acid. Isocyanic acid then reacts in the sense of a sulfonation to form chlorosulfonylisocyanate:

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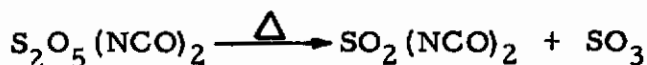
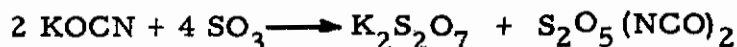


Sulfuryldiisocyanate could be prepared for the first time in good yield and purity by employing silver cyanate in accordance with

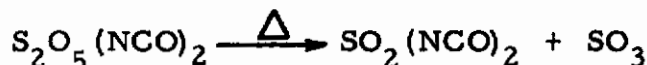
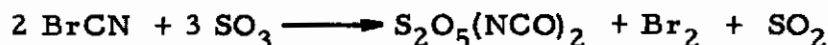


Sulfuryldiisocyanate is a colourless liquid of low viscosity which boils at 139° C/760 mm and solidifies at -5° C.

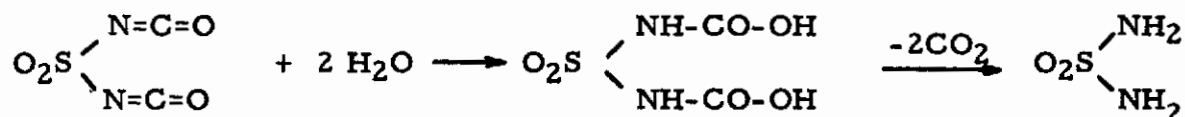
This reaction employing the silver salt is, however, too expensive for the preparation of larger quantities of the compound. A further convenient method of synthesis of the diisocyanate of sulfuric acid consists of reacting sulfur trioxide with potassium cyanate. This leads to the formation of potassium disulfate together with disulfuryldiisocyanate and this latter compound splits off sulfur trioxide upon being heated for longer periods of time at 140° C to yield sulfuryldiisocyanate



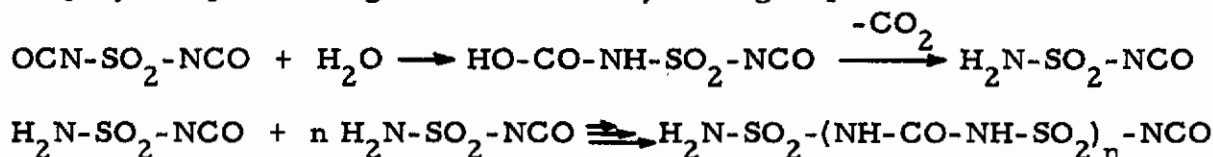
However, the reaction of sulfur trioxide with cyanogen bromide represents the most expedient method of preparation of $\text{SO}_2(\text{NCO})_2$. In this case, elementary bromine and sulfur dioxide are formed together with disulfuryldiisocyanate, whereupon pyrolytic fission can be carried out in the manner just described to produce, as before, sulfur trioxide and the diisocyanate of sulfuric acid:



The reactive behaviour of the diisocyanate is determined by the two isocyanate groups, which, as would be expected, react with all proton-active materials. With excess water, liberation of CO_2 occurs and sulfamide is formed in quantitative yield:



If, however, only 1 mole of water in acetonitrile is allowed to act upon the diisocyanate, amidosulfuric acid isocyanate is first formed. This substance is not very stable and it slowly undergoes a head-to-tail polymerization to form a sulfuryl urea polymer possessing a terminal isocyanate group:



The course of polymerization was measured kinetically and a result for the half life of amidosulfonic acid isocyanate of $T_{25}^0 = 623$ minutes was found.

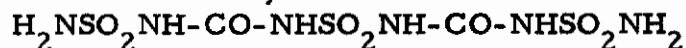
In the reaction of sulfuryldiisocyanate and of amidosulfonic acid isocyanate with alcohols and with amines, a large number of sulfo-urethanes and sulfo-ureas could be prepared. Further details in this respect cannot be included in this report.

The activation of the isocyanate group by the neighbouring SO_2 -group is so great that both sulfuryldiisocyanate and amidosulfonic acid isocyanate react with acid amides, although in general these amides are characterized by low proton activity. In this way, the reaction with sulfamide led to the formation of the following compounds:

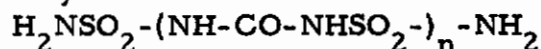
Urea disulfonic acid amide:



Sulfuryl-di-urea sulfuryl amide:

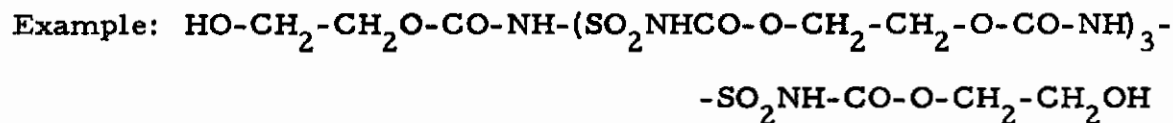
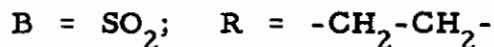
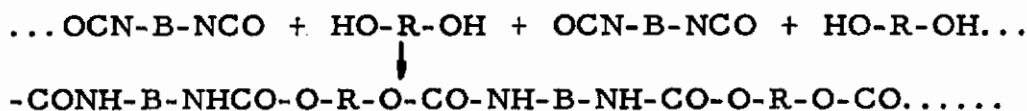


Polysulfuryl ureas:



In a similar manner, urea and thio-urea react very readily with both starting compounds. Unfortunately, however, polymers of this type are not very stable. As a result of the numerous SO_2 groups with their acidifying influence in the chain, all the compounds just mentioned hydrolyze rather easily.

Further experiments were conducted with the aim of increasing the stability towards hydrolysis by incorporating organic groups in the molecule. By reacting sulfuryldiisocyanate with ethylene glycol, we were able to obtain polymeric horn-like materials which were readily soluble in dimethylformamide and from which films could be prepared. However, the polymers are not resistant to prolonged treatment with boiling water and hydrolysis occurs in this case also. The course of synthesis is as follows:

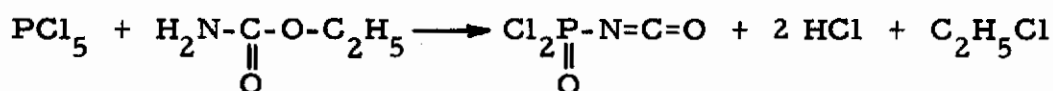


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We hope now to encounter superior properties in the corresponding phosphorus compounds. Phosphorus oxytriisocyanate will serve as starting material in these studies. This compound can be obtained in the reaction of phosphorus oxytrichloride with monomeric isocyanic acid in the presence of weak bases, although yields are poor.



Further research will be conducted with dichlorophosphorus oxyisocyanate, $\text{OPCl}_2(\text{NCO})$, which can be obtained in good yield from the reaction of phosphorus pentachloride with urethane according to A. V. Kirsanov:



1. R. Graf, Chem. Ber. 89.1071 (1956).

2. A. V. Kirsanov, Zhur. Obschei. Khim. 24.1033 (1954); C. A. 49.8787a (1955).